

CHARACTERIZATION AND DEPOSIT FORMING-TENDENCY OF POLAR COMPOUNDS IN CRACKED COMPONENTS OF GASOLINE. IDENTIFICATION OF OXIDIZED SULFUR COMPOUNDS.

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ABSTRACT

In order to evaluate the deposit forming-tendency of polar compounds in gasoline, one FCC component from a Venezuelan refinery was studied. The polar compounds were separated by column chromatography on alumina, using hexane, benzene, ethyl acetate and methanol as eluents, and their deposit forming-tendencies were determined by ISD apparatus. The ethyl acetate and methanol fractions showed high tendencies to form deposits. Identification of the different components of these fractions was intended by spectroscopic methods (IR, ^1H and ^{13}C -NMR and GC-MS) in subfractions obtained by further column and thin layer chromatographies. The main components were identified as mono- and dimethyl 2,3-dihydrobenzothiophene-S,S-dioxides in the ethyl acetate fraction, and mono- and dimethyl benzothiophene-S-oxides in the methanol fraction. This is the first report on the presence of this type of compound in gasoline components, and on their role as deposit-forming promoter.

INTRODUCTION

The role of oxidized compounds in deposit formation in the induction system of gasoline engines has been reported. This type of compounds have a natural affinity for metal surfaces and may react vigorously on the surface forming high deposit levels. Taniguchi (1) found that polar materials are implicated in Port Fuel Injector (PFI) deposit formation. Laboratory test showed that deposit formation was reduced when polar compounds were removed from unstable gasolines (2). Alcohol and catalytic cracked components in the fuel have been found to increase inlet valve deposits (3). The thermal decomposition of oxidized polar compounds, such as ketones, alcohols, carboxylic acids and others, contained in the fuel or formed by oxidation of fuel olefins increased of the ISD deposit formation (4).

This study reports the characterization of two sulfur-rich and high polar fractions obtained by adsorption chromatography a cracked gasoline component and their contributions to deposit formation.

EXPERIMENTAL

Separation

The cracked gasoline component FCC-1 was subjected to acid-base extraction and adsorption chromatography on a column packed with neutral aluminum oxide, according to a previously described procedure (5). The material retained on the column was eluted with one gallon each of the following solvents: hexane, benzene, ethyl acetate and methanol. These fractions were evaporated under reduced pressure ($T < 50^\circ\text{C}$) under an inert atmosphere.

Instrumentation

The carbon-13 and hydrogen-1 NMR spectra were recorded with a Bruker MSL-300 or an ACP-400 spectrometer at room temperature, using CDCl_3 as solvent and TMS as internal standard. Samples were contained in 5 mm i.d. nmr cells.

The mass spectra of the ethyl acetate fraction was obtained with a Hewlett Packard 5995A GC/MS apparatus, equipped with a 60 m x 0.32 mm i.d. (0.25 μm film) DB-1 Megabore column, programmed from 50-200°C at 5°C/min, using helium as carrier gas. The GC/MS of the methanol fraction was obtained with a Ruska Laboratories apparatus, equipped with a 30 m x 0.32 mm i.d. (0.25 μm film) DB-5 column with the same temperature program.

Infrared spectra were recorded with a Perkin-Elmer model 1310. The samples were prepared as thin films on NaCl plates.

Total nitrogen and sulfur contents were determined by chemiluminescence and x-ray (ASTM D-2622) methods.

The subfraction R-1-D was analyzed by GC using a Hewlett Packard 5890A apparatus equipped with a sulfur-selective chemiluminescence detector (Sievers 350B), under similar chromatographic conditions as those used for the GC/MS analyses.

In order to evaluate the deposit-forming tendency of the isolated fractions, 1000 ppm solutions of each fraction in the original FCC-1 sample were tested in an Induction System Deposit (ISD) apparatus (6). This apparatus simulates intake valve deposit formation. Fuels with a high deposit-forming tendency produce > 2 mg/100ml fuel.

RESULTS AND DISCUSSION

Ethyl acetate fraction.

The elemental analyses of the ethyl acetate fraction showed a high level of sulfur (2.9%) and a low level of nitrogen (0.2%). The ISD evaluation showed a high deposit-forming tendency (2.8 mg/100ml).

The IR spectrum of this fraction showed bands at 3600-3400, 2900-2800, 1750-1650 y 1150-1050 cm^{-1} , assignable to O-Hst, C-Hst (alifatic), C=Ost y C-Ost, respectively.

The ^1H -NMR spectrum showed strong signals at 8-7 ppm (ArC-H), 2-2.6 ppm (Ar-CH₃ and/or H of saturate cycles) and 1.5-0.8 ppm (-CH₂-) and lower intensity signals at 5-6 ppm =C-H, 3-3.5 ppm -CH-X (X=O or N or S=O) and/or -CH₂-C=O.

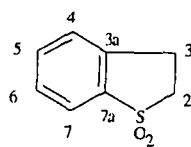
The ^{13}C -NMR showed very different kind of signals. The more important were located at 120-142 ppm (ArC and/or =C-H), 200-210 ppm (R-C=O, R-O-C=O and/or H-C=O), 172-170 ppm (HO-C=O), 62-64 ppm (HO-CH₂- and/or R-O-CH₂-), 50-55 ppm (-CH₂-C=O in saturated cycles, -O-CH₃ or -CH₂-S=O_x), 40-48 ppm (-CH₂- y -CH saturates cycles) and 10-30 ppm (-CH₂)_x and/or Ar-CH₃.

This fraction was subjected to adsorption chromatographic on a column packed with silica gel. The material retained on the column was eluted with mixtures of benzene, benzene-chloroform and chloroform-methanol, obtaining three fractions: R-1-A (7.7%), R-1-B (17.8%) and R-1-D (74.5%).

The subfractions R-1-A and R-1-B were identified as mixture of dimethylnaphthalenes and phthalic acid derivatives, respectively.

The carbon-13 NMR spectrum (Fig.1) of the major fraction R-1-D showed strong signals in the 50-53 ppm zone, assignable to -CH₂-C=O of saturated cycles, -O-CH₃ or -CH₂-S=O_x (n=1,2 and x=1,2). A DEPT experiment showed that these signals corresponded to -CH₂- groups. The GC analysis of this subfraction with a sulfur-selective detector showed the presence of sulfur compounds.

A detailed study of the carbon-13 NMR chemical shift data of this subfraction indicated the presence of 2,3-dihydrobenzothiophene, S,S-dioxide (7):



| CARBON N° | OBSERVED δ (ppm) | REPORTED δ (ppm) |
|-----------|-------------------------|-------------------------|
| 2 | 50.6 | 50.6 |
| 3 | 25.4 | 25.3 |
| 4 | 128.7 | 128.8 |
| 5 | 133.4 | 133.4 |
| 6 | 127.3 | 127.2 |
| 7 | 121.3 | 121.5 |
| 3a | 137.2 | 137.2 |
| 7a | 138.9 | 138.9 |

The GC/MS chromatogram (Fig.2) showed ten strong signals. Only one of these peaks was identified as 2,3-dihydrobenzothiophene, S,S-dioxide (m/e 168) according to the NIST Library mass spectral data (N° 12353) and in agreement with our ^{13}C -NMR results. The M⁺ of the other signals: 182 (168+14) and 196 (168+14+14) suggested the presence of methyl- and dimethyl- 2,3-dihydrobenzothiophene, S,S-dioxide. Figures 3 and 4 show probable fragmentation ways of these compounds. Other compounds were identified as methyl and dimethyl indanones, present in minor concentrations.

Methanol fraction.

The elemental analyses of the methanol fraction showed the highest level of sulfur (3.5%) of all the obtained fractions and a low level of nitrogen (0.2%). The ISD evaluation showed also the highest deposit-forming tendency (6.1 mg/100ml).

The IR spectrum of methanol fraction showed bands at 3600-3400, 2980-2880, 1750-1650 and 1150-1050 cm^{-1}

assignable to O-Hst, C-Hst (alifatic), C=Ost and C-Ost or S=Ost, respectively.

The hydrogen-1 NMR spectrum showed strong signals at 8-7 ppm (ArC-H), 2-2,6 ppm (Ar-CH₃ and/or H of saturated cycles) and 1,8-1,0 ppm (-CH₂)_x-, and lower intensity signals at 5-6 ppm (=C-H) and 3-4 ppm (-CH-X X=O or N or S=O and/or -CH₂-C=O).

The carbon-13 NMR spectrum showed many different types of signals. The more important were located at 115-158 ppm (ArC and/or -C=C-H), 200-210 ppm (R-C=O), 173,6 ppm (HO-C=O or RO-C=O), 76-64 ppm (-CH-OH), 50-53 ppm (-CH₂-C=O in saturated cycles and/or O-CH₃), and 12,7-20,9 ppm (-CH₂- and/or Ar-CH₃).

This fraction was subjected to adsorption chromatography on a column packed with silica gel. The material retained on the column was eluted with mixtures of chloroform-methanol, obtained one major fraction R-2-B (73.3%).

The IR spectrum of this fraction showed a strong band located at 1060-1020 cm⁻¹ attribute to S=Ost in sulfones. A detailed study of the carbon-13 NMR chemical shift data of this subfraction indicated the presence of 1- and 2-methyl benzothiophene, S-oxide and 1,2-dimethyl benzothiophene, S-oxide (Table 1).

The GC/MS analysis indicated 1- and 2-methyl benzothiophene, S-oxide (m/c 164), confirming the previous carbon-13 NMR assignments (8). The M⁺ of the others signals: 178 (164+14) suggested the presence of dimethyl benzothiophene, S-oxide. Fig. 5 show probable fragmentation ways for these compounds. Other compounds, present in minor concentrations, were identified as benzothiophene, methyl- and dimethyl-benzothiophenes.

To our knowledge, this is the first report demonstrating the presence of this type of compounds in gasoline fractions, and revealing the importance as promoter in the formation of deposit..

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Table 1. Carbon-13 NMR chemical shifts of subfractions R-2-B fraction (Observed vs. Reported⁽⁷⁾ values).

| Carbon | Reported | Observed |
|--------|----------|----------|
| 2 | 150.6 | 149.8 |
| 3 | 128.7 | 128.7 |
| 4 | 127.6 | 127.5 |
| 5 | 132.0 | 131.9 |
| 6 | 123.7 | 123.7 |
| 7 | 126.1 | 126.0 |
| 3a | 138.2 | 138.0 |
| 7a | 144.8 | 145.2 |
| 2-Me | 12.8 | 12.8 |

| | | |
|------|-------|-------|
| 2 | 132.1 | 132.0 |
| 3 | 145.2 | 145.2 |
| 4 | 128.7 | 128.9 |
| 5 | 131.8 | 131.6 |
| 6 | 122.5 | 122.6 |
| 7 | 125.8 | 125.8 |
| 3a | 138.5 | 138.3 |
| 7a | 145.9 | 145.5 |
| 3-Me | 14.1 | 14.0 |

| | | |
|------|-------|-------|
| 2 | 143.7 | 143.9 |
| 3 | 136.5 | 136.7 |
| 4 | 127.6 | 127.5 |
| 5 | 131.9 | 131.9 |
| 6 | 121.6 | 121.6 |
| 7 | 125.7 | 125.5 |
| 3a | 139.9 | 139.8 |
| 7a | 142.9 | 143.0 |
| 2-Me | 10.6 | 10.4 |

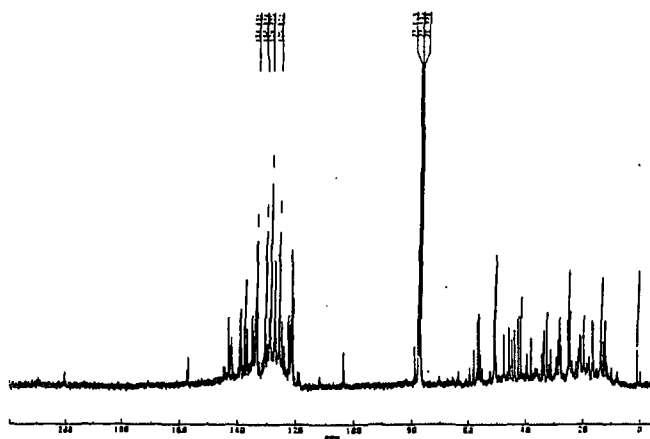


Fig.1 Carbon-13 NMR spectrum of fraction R-1-D.

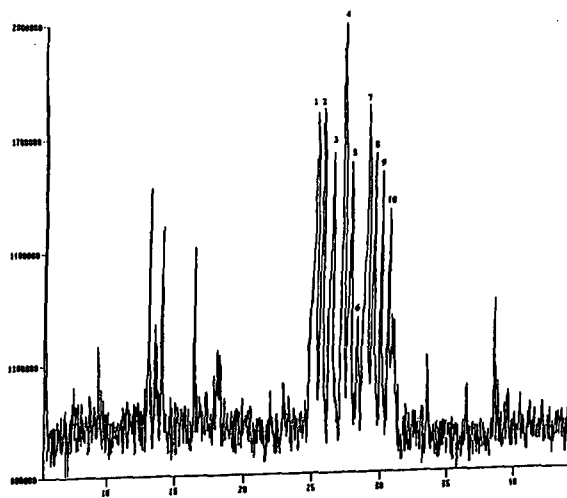


Fig.2 GC/MS chromatogram of fraction R-1-D.

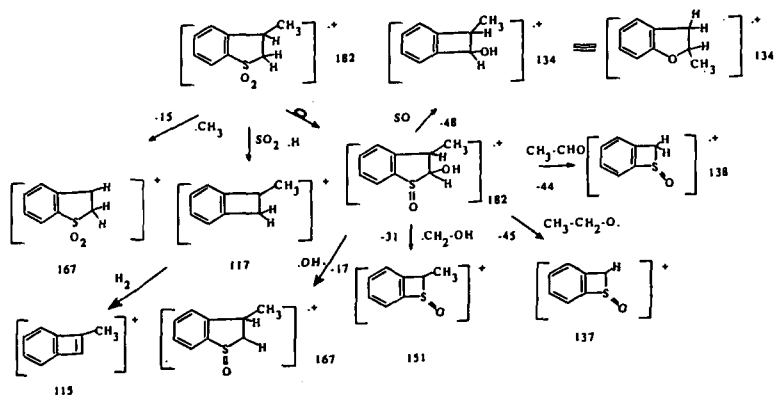


Fig.3 Probable mass fragmentation of methyl-2,3-dihydrobenzothiophene, S,S-dioxide.

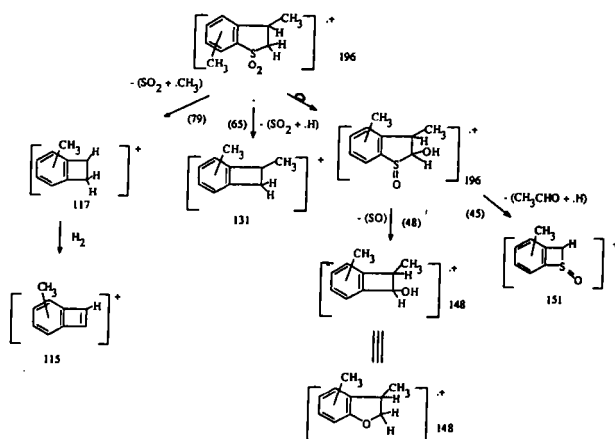


Fig.4 Probable mass fragmentation of dimethyl-2,3-dihydrobenzothiophene, S,S-dioxide.

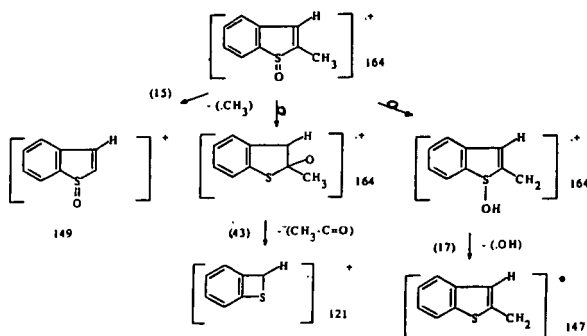


Fig.5 Probable mass fragmentation of methyl benzothiophene, S-oxide.